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Project Summary

Chemical Transformations in Acid Rain: Volume I. New Methodologies for Sampling and Analysis of Gas-Phase Peroxide

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Roger L. Tanner

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New methodologies for sampling and analysis of gas-phase peroxides (H_2O_2 and organic peroxides) using (a) diffusion denuder tubes and (b) gas-to-liquid transfer with prior removal of ozone have been investigated. The purpose was the development of an interference-free method for determining H_2O_2(g) in ambient air. A denuder approach using ferrous (1, 10-phenanthroline)-coated tubes was unsuccessful for, although H_2O_2 was removed, the capacity was low and ozone was also removed, possibly through surface decomposition to H_2O_2 and its radical precursors. Gaseous peroxide in compressed airstreams could be collected in impingers without artifact formation from surface ozone decomposition if O_3 was first removed by gas-phase titration with nitric oxide.

This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The purpose of this research task was to develop fundamentally new methods for sampling and analysis of gas-phase hydrogen peroxide (H_2O_2) and organic peroxides, if possible, through the use of diffusion-denuder tubes. In addition, sampling methods for H_2O_2 using gas-to-liquid transfer and capable of avoiding *in situ* production of H_2O_2 from ozone (O_3) decomposition and other processes were studied. The goal of the research was an interference-free method for gas-phase peroxides with 0.1 ppb limit of detection and 15 min time resolution.

Much analytical effort has been expended in the past few years in measuring gaseous and aqueous H_2O_2 following the recognition that H_2O_2 could oxidize dissolved S(IV) rapidly throughout the pH range of rain, cloud and fog waters. Furthermore, the high solubility of H_2O_2 in water led to significant H_2O_2 concentrations in cloudwater. Methods for determining liquid-phase H_2O_2 have been developed using several approaches: luminol chemiluminescence, p-hydroxyphenylacetic acid dimer fluorescence, scopoletin fluorescence quenching and peroxyoxalate chemiluminescence. Attempts to measure gas-phase hydrogen peroxide by collection in impingers or by other dissolution techniques have been shown to be generally unreliable due to the *in situ* formation of hydrogen peroxide from low-solubility constituents of ambient air during collection by impingers. It is suspected that surface-initiated ozone decomposition via HO_2^- and O_2^- intermediates is the likely mechanism of "artifact" H_2O_2 formation.

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Two possible research approaches for artifact-free sampling of H_2O_2(g) were investigated in this project: selective, reactive sampling onto a coated denuder tube, employing H_2O_2 redox chemistry and suppression of *in situ* H_2O_2 formation by selective removal of ozone.

This study describes a denuder approach using ferrous (1,10-phenanthroline) coated tubes that was successful: the capacity for H_2O_2 was low and ozone was also removed, possibly through surface decomposition for H_2O_2 and its radical precursors. However, the study also documents that gaseous peroxide in compressed airstreams can be collected in impingers without artifact formation from surface ozone decomposition if O_3 is first removed by gas-phase titration with nitric oxide.

Experimental

Experiments in this task were conducted by using a system in which gas-phase hydrogen peroxide was reproducibly generated in the 1-500 ppbv range by multiple dilutions with compressed air, with facilities to subsequently humidify the air and add ozone and nitric oxide to the diluted airstream (see Figure 1). Parallel airstreams were then formed with appropriate mixing chambers, and peroxide was collected in parallel series of 2 or 3 midget impingers that were followed by flow meters, charcoal traps for ozone and H_2O_2, and a common, selectable inlet line to the ozone analyzer. Diffusion denuder tubes containing coatings of Fe(II)-1, 10-phenanthroline were tested in experiments by placing them in the flow streams after division at points A and B, just prior to impingers 1-1 and 2-1, respectively. Aqueous H_2O_2 in each of the six impingers was analyzed after each experiment using the POHPAA fluorescence method by sample injection into a flow injection system.

For the most of the experiments conducted in this task, an alternate, manually operated "stopped-flow" approach to aqueous H_2O_2 analysis was used. In this approach, three volumes of sample were mixed, with one volume of peroxidase/POHPAA/EDTA solution in pH 8.5 TRIS buffer. The premixed sample was allowed to standard for 2-3 min, and then an aliquot was injected directly into the fluorimeter flow cell for analysis. The flow cell was rinsed out thoroughly with TRIS buffer between injections. Extensive washing of the sample lines in contact with catalase solution was required before reuse.

Results and Discussion

Considerable effort was expended to improve the POHPAA fluorescence technique for aqueous-phase peroxide. These efforts were required because low levels of peroxide would have to be analyzed for passive denuder-collection H_2O_2 samples or for artifact-free impinger collections (if such could be achieved). Without the improved analytical sensitivity attained by these efforts, the stated goals of this task (0.1 ppbv, 15 min time resolution) would not have been possible. The final limit of detection achieved during this effort was 0.3 ppb aqueous (~ 0.01 μM). This sensitivity was just barely adequate to attain the task goal for the artifact-suppression or denuder approaches.

Denuder Tube Sampling

Pyrex denuder tubes, 0.6 cm OD by 30 cm long, were coated with ferrous-(1, 10-phenanthroline)-sulfate solution in methanol. They were then placed in the parallel airstreams downstream from the mixing chamber and, in the case of line 2, after the addition of NO in N_2 to the airstream. Various admixtures of compressed air and ozone and/or H_2O_2 were passed through the denuders. Nitric oxide (6.2 ppm after dilution) was added to line 2 and the apparent H_2O_2 in each of impingers 2-1 through -3 and 1-1 through -3 (see Figure 1) was determined using the POHPAA fluorescence technique. Fourteen experiments were conducted to test the denuder sampling technique. The results obtained suggested the following:

(1) Ferroin-coated denuder tubes of the type tested have limited capacity for H_2O_2 removal, but they also remove

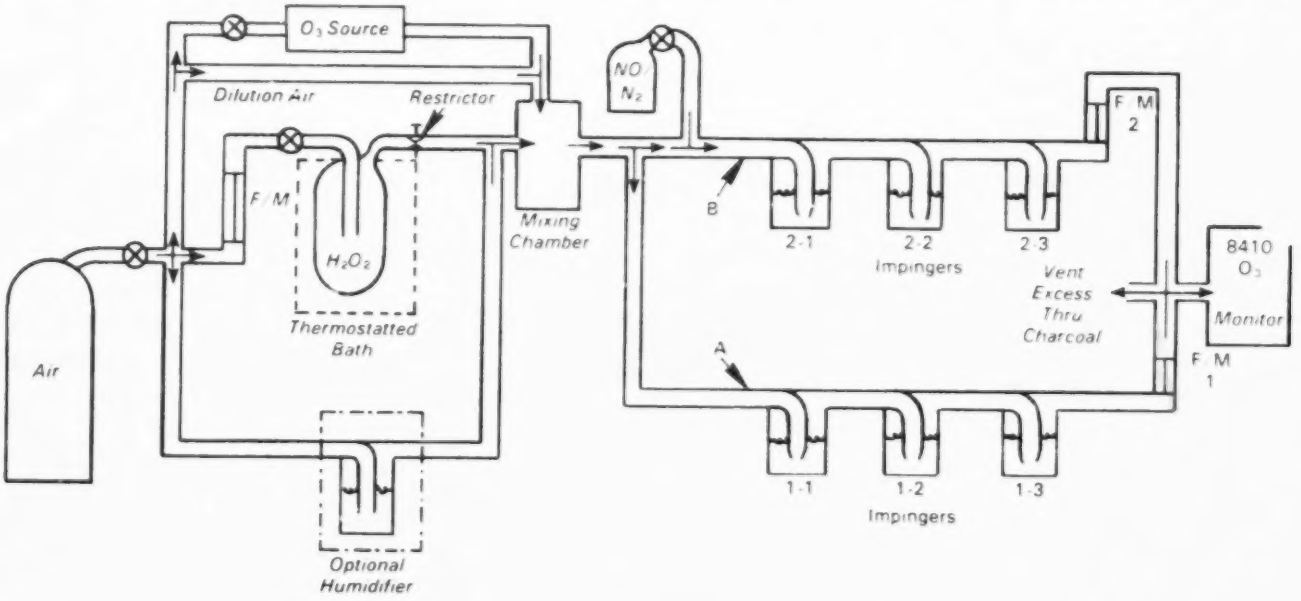

Figure 1. *Modified apparatus for H_2O_2 generation and impinger collection*

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O_3 at continuously decreasing efficiency.

(2) Ferroin-coated denuders do not prevent artifact H_2O_2 formation in impingers downstream of the denuder.

(3) It appears that ozone reacting on the denuder surface may generate artifact H_2O_2 on partially exhausted denuder tubes.

We do not wish to assert that all iron(II) complexes would exhibit the same behavior when used as denuder coatings as did ferroin, but only that the denuder approach as defined was heretofore unsuccessful in removing H_2O_2 quantitatively. In addition, complications are introduced because of co-removal of ozone and the likely co-reaction with the ferroin.

Gas-to-Liquid Sampling After O_3 Removal

As noted above, previous observations have suggested that artifact H_2O_2 formed in gas-to-liquid sampling using impingers or other approaches seems to be related to levels of ozone and one or more other air constituents. As a result, sampling approaches in which ozone is selectively removed from the sampled air may be successful in eliminating the artifact formation of H_2O_2 while simultaneously transmitting H_2O_2 at high, reproducible efficiency to an aqueous solution for POHPAA analysis of H_2O_2. Unreported data suggest that the amount of H_2O_2 formed in bubblers is non-linearly related to O_3 concentration in sampled air, but since O_3 reaction on the bubbler surfaces appears to be the initial and limiting step in artifact H_2O_2 formation, removal of O_3 prior to sampling should effectively eliminate the process.

The evidence that titration with excess NO removes artifact H_2O_2 formation in impinger collection of H_2O_2 is shown in Table 1. Hydrogen peroxide (calculated to be 28 ± 2 ppb in stream 1 and 22 ± 4 ppb in stream 2) was admitted without O_3 or NO in Expts. 1 and 2; peroxide was found in roughly equal amounts in bubblers 1-1 and 2-1. No peroxide was found in subsequent bubblers. Ozone at 327 ± 13 ppb was admitted to the system in Expts. 3 through 9, with NO (6.2 ppm) present in stream 2 only for Expts. 4 through 9. In Expt. 3, addition of ozone alone to both streams produced H_2O_2 in all impingers with most being found in impinger 1 of each stream. Addition of ozone + H_2O_2 mixtures to stream 1 and $O_3/H_2O_2/NO$ to stream 2 (Expts. 4, 5, and 9) produced additional peroxide in all stream 1 bubblers consistent with the results of Expt. 3, but no peroxide was formed in stream 2 bubblers sampling NO-containing air.

The amount of artifact H_2O_2 sampled from O_3-containing airstreams was variable, and appears to be reduced in Expts. 5 to 9 in comparison to Expts. 1 to 4. Indeed, no artifact H_2O_2 was formed in impingers 2-2 and 2-3 during Expts. 6 to 8. In contrast, only in Expt. 6 was a small amount of H_2O_2 found in the $O_3/NO/air$-stream. This could be due to inadequate mixing of NO with the ozone/airstream, but is more likely the result of desorption of H_2O_2 retained in the mixing chamber from the previous experiment. Nevertheless, the preponderance of evidence suggests that ozone is removed sufficiently fast that no measurable artifact H_2O_2 is formed.

Artifact H_2O_2 is formed in variable amounts when an airstream containing about 300 ppb O_3 is sampled. Collected amounts correspond to about 3-15 ppb of gaseous H_2O_2 in the first bubbler and roughly an order of magnitude lower in subsequent bubblers. This differs somewhat from results reported by others in which roughly equal amounts of peroxide were formed in subsequent bubblers, and indeed, it is different from our own early results, suggesting that the extent of the process in which artifact H_2O_2 is formed is quite dependent on the presence of other atmospheric constituents in addition to O_3. That these constituents may differ widely in their aqueous solubility is suggested by the low production rate of artifact H_2O_2 in impingers 2 and 3 compared to impinger 1 for the experiments summarized in Table 1.

Conclusions

The research approaches investigated in this task for artifact-free sampling of $H_2O_2(g)$ included selective, reactive sampling onto a coated denuder tube, employing H_2O_2 redox chemistry and suppression of *in situ* H_2O_2 formation by selective removal of ozone.

A denuder approach was attempted employing Fe(II)-1,10-phenanthroline-coated glass tubes. Hydrogen peroxide was removed by such tubes but collection efficiencies less than calculated values were observed even with relatively fresh tubes. This suggested that surface depletion of sorption sites was reducing the capacity of *dry* coating on the diffusion tube. In addition, ozone was removed to a significant extent by the Fe(II)-phenanthroline denuder tubes, which indicated a lack of specificity for H_2O_2 and raised the spectre of surface decomposition of O_3, possibly to gas-phase HO_2 and/or H_2O_2.

Table 1. *Collection of H_2O_2 from Ozone-Containing and Ozone-Free Air Streams*

Experiment No.	H_2O_2 (μM) in Sampled Gas Stream 1			H_2O_2 (μM) in Sampled Gas Stream 2		
	Composition	Bubbler 1	Ave, Bubbler 2 + 3	Composition	Bubbler 1	Ave, Bubbler 2 + 3
1	H_2O_2/Air	0.58	ND*	H_2O_2/Air	0.56	ND
2	"	0.55	"	"	0.39	ND
3	O_3/Air	0.36	0.022	O_3/Air	0.31	0.014
4	$O_3/H_2O_2/Air$	0.96	0.018	$O_3/H_2O_2/NO/Air$	0.52	ND
5	"	0.63	0.016	"	0.45	ND
6	O_3/Air	0.15	ND	$O_3/NO/Air$	0.026	ND
7	"	0.044	ND	"	ND	ND
8	"	0.047	ND	"	ND	ND
9	$O_3/H_2O_2/Air$	0.69	0.060	$O_3/H_2O_2/NO/Air$	0.50	ND

**ND = none detected (≤ Blank)*

Gas Phase Concentrations:

[Ozone] = 327 ± 13 ppb (Expts. 3-9)

$[H_2O_2]$ = 28.0 ± 2.0 ppb (Stream 1); 22.2 ± 3.6 ppb (Stream 2)

[NO] = 6.2 ppm

Sampling Conditions:

Air sampled for 30 min 0.50 L/min in each line.

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Thus, removal of H_2O_2 onto denuders by nominally H_2O_2-specific chemisorption does not appear to offer significant advantages over gas-to-liquid sampling for gaseous H_2O_2 analysis.

Suppression of *in situ* production of H_2O_2 in gas-to-liquid sampling (bubblers, impingers) by upstream titration of the ozone in the sampled airstream has been successfully demonstrated for cases in which compressed air is used. Gaseous hydrogen peroxide was collected completely (>99%) in the first bubbler whereas confluent ozone produced measureable peroxides in the second and third bubblers; no peroxide was observed in the second and third bubblers for those experiments in which O_3 (100-300 ppb) was titrated by 6 ppm NO prior to bubbler collection. The addition of 6 ppm NO does not significantly interfere with POHPAA analysis of collected aqueous H_2O_2.

Roger L. Tanner is with Brookhaven National Laboratory, Upton, NY 11973.
***Marcia C. Dodge** is the EPA Project Officer (see below).*
The complete report, entitled "Chemical Transformations in Acid Rain: Volume I. New Methodologies for Sampling and Analysis of Gas-Phase Peroxide," (Order No. PB 85-174 425/AS; Cost: $8.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Atmospheric Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

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